



Doping, Dopants & Carrier Dynamics in Wide Gap Semiconductors Workshop

MEETING PROGRAM & ABSTRACT BOOK

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**April 2-6, 2000
Copper Mountain Resort
Copper Mountain, CO**

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Doping, Dopants & Carrier Dynamics in Wide Gap Semiconductors Workshop Schedule

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Note: All Workshop Sessions/Luncheons will be hosted in the Copper Commons Conference Center.

Welcoming Reception, Sunday evening, April 2, 2000, 7:30 - 9:30 p.m.

Speaker Name/Presentation Title	
Monday, April 3rd, Continental Breakfast: 7:30 - 8:00 a.m.	
Piccadilly A Room	
Session 1: Bulk and Epitaxial Growth	
Monday Morning	
8:00 a.m. - Welcome & Orientation – Fred Schubert	
8:10 a.m. - 8:20 a.m. (Scene-setter)	Colin Wood: ONR's Funded Efforts to Get More Holes and Make Them Move
8:20 a.m. - 8:40 a.m.	Henryk Temkin: Doping in Gas Source Molecular Beam Epitaxy of GaN/AlGaIn
8:40 a.m. - 9:00 a.m.	Enrique Calleja: Growth and Doping of III-Nitrides by MBE
9:00 a.m. - 9:20 a.m.	Loren Pfeiffer: Comparison of Si Doping in GaN MBE Grown by Plasma Nitrogen and Molecular Ammonia
9:20 a.m. - 9:40 a.m.	Klaus Ploog: P-type Doping of GaN and Related Alloys
9:40 a.m. - 10:00 a.m.	Russell Dupuis: P- and N-type Doping in AlGaIn and GaN Films Grown by Metalorganic Chemical Vapor Deposition
Break: 10:00 a.m. - 10:20 a.m.	
10:20 a.m. - 10:40 a.m.	Joan Redwing: The Effect of Silicon Doping on the Structural and Electrical Properties of AlGaIn/GaN HEMT Structures
10:40 a.m. - 11:00 a.m.	Volker Wagner: Structural Defect Characterization of ELO GaN Hydride VPE Layers
11:00 a.m. - 11:20 a.m.	Tom Kuech: Growth and Characterization of Bi-doped GaN Epilayers and GaN:Bi Lateral Epitaxial Overgrowth by Metal Organic Vapor Phase Epitaxy
11:20 a.m. - 11:40 noon	Mike Mazzola: Precision SiC EPI Growth for Advanced FET Development
11:40 p.m. - 12:00 noon	Alan Doolittle: Acceptor Dopants in III-Nitrides
Lunch: 12:00 noon - 1:00 p.m. in The Pub, followed by spontaneous discussions.	
Session 2: Doping Elements, Doping Process, and Doping Theory	
Monday Evening	
7:00 p.m. - 7:30 p.m. (Scene-setter)	Tetsuya Yamamoto: Control of Valence States of ZnO and AlN by Codoping Method
7:30 p.m. - 7:50 p.m.	Tom Myers: Magnesium and Beryllium Doping During rf-plasma MBE Growth of GaN
7:50 p.m. - 8:10 p.m.	Jaime Freitas: Donor and Acceptors in Undoped and Si-doped Heteroepitaxial GaN Layers
8:10 p.m. - 8:30 p.m.	Marcus Scherer: Influence of Multiple-Step Annealing on P-type Conductivity and Contact Behavior
8:30 p.m. - 8:50p.m.	William Schaff: P-doping of III-Nitrides
8:50 pm. - 9:10 p.m.	Pierre Gibart: Doping of GaN with Mg, Ca, and C During MOVPE

Speaker Name/Presentation Title	
Tuesday, April 4th, Continental Breakfast: 7:15 - 8:00 a.m.	
Piccadilly A Room	
Session 3: Dopant Characterization and Doping Theory	
Tuesday Morning	
8:00 a.m. - 8:30 a.m. (Scene-setter)	Chris Van de Walle: New Insights in P-type Doping of III-Nitrides
8:30 a.m. - 8:50 a.m.	Les Eastman: Acceptor Activation in Ga(Al)N and the Effect of Dislocations on Electronic Transport in GaN
8:50 a.m. - 9:10 a.m.	Bo Monemar: Study of Magnetic Resonance (ODMR) and Optical Properties of Shallow Acceptors in GaN
9:10 a.m. - 9:30 a.m.	Brian Skromme: Investigation of Dopants in GaN by Ion Implantation and Optical Spectroscopy
9:30 a.m. - 9:50 a.m.	Wladek Walukiewicz: Doping Limitations in Wide-Gap Semiconductors
Break 9:50 a.m. - 10:00 a.m.	
10:00 a.m. - 10:20 a.m.	Werner Goetz: Hall-Effect Characterization of Mg-Doped GaN and Al _x Ga _{1-x} N ($x \leq 0.17$)
10:20 a.m. - 10:40 a.m.	Cole Litton: Native Point Defects in ZnO Substrates: Electrical and Optical Properties
10:40 a.m. - 11:00 a.m.	Bruce Wessels: Compensation Mechanisms in P-Type GaN
11:00 a.m. - 11:20 a.m.	Tadeusz Suski: Electrical and Optical Characterization of Dopants in Group-III-Nitrides Under High Pressure
11:20 a.m. - 11:40 a.m.	Jacques Pankove: Shallow Acceptors in III-Nitrides
Lunch: 11:45 a.m. - 12:45 p.m. Followed by spontaneous discussions	
NOTE: Tuesday night = Reception: 6:00 - 7:00 p.m.; Sleigh Ride to Dinner: 7:00 - 7:30; Dinner: 7:30 - 9:30 p.m.	
Wednesday, April 5th, Continental Breakfast: 7:15 - 8:00 a.m.	
Piccadilly A Room	
Session 4: Polarization and Piezo Effects and Novel Structures	
Wednesday Morning	
8:00 a.m. - 8:30 a.m. (Scene-setter)	Michael Shur: P-type and N-type Polarization Doping in GaN-based Heterostructures
8:30 a.m. - 8:50 a.m.	Oliver Ambacher: Polarization Induced Effects in P-Doped Al _x Ga _{1-x} N and AlGaIn/GaN Heterostructures
8:50 a.m. - 9:10 a.m.	Peter Asbeck: The Influence of Polarization Effects on Impurity Incorporation in Nitride Materials
9:10 a.m. - 9:30 a.m.	M. Asif Khan: Doping Studies of Quaternary AlGaInN Materials and AlGaInN/InGaIn Heterostructures and Quantum Wells
9:30 a.m. - 9:50 a.m.	Umesh Mishra: Superlattice Doping: Pros and Cons
9:50 a.m. - 10:10 a.m.	Fred Schubert: Current Results and Future Potential of Doped p-type AlGaIn/GaN Superlattices
Break: 10:10 a.m. - 10:20 a.m.	

Speaker Name/Presentation Title	
Wednesday, April 5th	
Session 5: Carrier Dynamics, Carrier Transport, and Devices	Wednesday Morning
10:20 a.m. - 10:50 a.m. (Scene-setter)	Brian Ridley: Electron Transport in GaN/AlGaN Structures
10:50 a.m. - 11:10 a.m.	Kevin Brennan: High Field Transport Calculations in 4H-SiC
11:10 a.m. - 11:30 a.m.	Frederick Long: Laser Spectroscopy of Doping and Carrier Dynamics in WBG Semiconductors
11:30 a.m. - 11:50 a.m.	Takeshi Uenoyama: Carrier Dynamics in Schottky Diodes
11:50 a.m. - 12:10 p.m.	Simon Verghese/Rich Molnar: HVPE-grown GaN Avalanche Photodiodes
Lunch: 12:10 p.m. – 1:10 p.m.	
Session 5: Continued	Wednesday Afternoon
1:10 p.m. - 1:30 p.m.	John Zavada: Visible and Infrared Luminescence from Er-doped GaN films
1:30 p.m. - 1:50 p.m.	Marshall Nathan: Doped GaN Quantum Dots
1:50 p.m. - 2:10 p.m.	Andrei Osinsky: P-type Superlattice Doping: Material Characteristics Pertaining to Bipolar Devices
Session 6: Defects, Deep Levels, Ordering and Other Doping Issues	Wednesday Afternoon
2:10 p.m. - 2:40 p.m. (Scene-setter)	Zuzanna Liliental-Weber: Influence of Dopants on Defect Formation in GaN; Bulk and MOCVD Grown Samples
Break: 2:40 – 2:50 p.m.	
2:50 p.m. - 3:10 p.m.	H. Katayama-Yoshida: Valence Control by Codoping in Wide Band-gap Semiconductors (GaN, AlN, ZnSe, ZnO): Prediction vs. Experiment
3:10 p.m. - 3:30 p.m.	Trevor Tansley: Recent Progress in the Low Temperature Growth of GaN by combined Laser Induced and Plasma Assisted Chemical Vapor Deposition
3:30 p.m. - 3:50 p.m.	Joerg Neugebauer: Defects and Doping in Group-III Nitrides
3:50 p.m. - 4:10p.m.	Marcy Berding: Native Defects in SiC
Thursday, April 6th: Wrap-up Session w/Continental Breakfast (8:00 am - 10:00 am)	
Piccadilly A Room	
The Wrap-up session provides an opportunity for participants to gather to summarize the findings/technical information shared throughout the week. It's also the last opportunity to obtain answers to questions that time may not have allowed during the session. Please plan to join us!	

ONR's Funded Efforts to get More Holes and Make them Move

Colin Wood
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ONR's power microwave plans include use of Nitride based bipolar transistors. Unless p-type conductivities can be increased an order of magnitude, it is unlikely that such devices will be available with sufficient performance. This presentation will briefly discuss ideas and progress of ONR awards to investigate possible alternative approaches for increased p-type conductivity in GaN, and its alloys.

Doping in Gas Source Molecular Beam Epitaxy of GaN/AlGaN

Henryk Temkin

Abstract not available at time of publication.

Growth and Doping of III-Nitrides by MBE

E. Calleja, M.A. Sánchez-García, J.L. Pau, F. Naranjo, A. Jiménez, and E. Muñoz

Dpt. Ingeniería Electrónica, ETSI Telecomunicación, Univ. Politécnica, Madrid, Spain.

The growth and properties of Ga(Al)N layers on Si(111), sapphire, and GaN-templates by plasma-assisted MBE are revised and compared. Control of layer morphology, from columnar whisker-like, to compact material, as a function of the III/V ratio, is analyzed. GaN nanocolumns, with diameters ranging from 600 to 1500 Å, are consistently grown under nominally N-rich conditions. "Ga-balling" generation, due to the reduced surface diffusion of Ga-adatoms by excess nitrogen, seems to be the driving force for columns formation.

Undoped, compact GaN layers, grown by MBE on Si(111) and sapphire, generally show a lower crystal quality than that of layers grown by MOVPE. However, GaN layers grown by MBE on GaN MOVPE templates have better properties than the templates themselves in terms of residual n-type conductivity, carbon contamination, and reduced Yellow Luminescence.

N-type doping with Si provides electron densities up to $2 \times 10^{19} \text{ cm}^{-3}$ in GaN and $8 \times 10^{19} \text{ cm}^{-3}$ in AlGaIn (40%). Si-doping of GaN layers grown on Si(111) is found to modify the growth mode leading to a reduction of the threading dislocation density by one order of magnitude. In addition, these layers exhibit an increase of the biaxial tensile strain with the Si-doping.

P-type doping with Be generates the shallowest acceptor level ($\cong 90 \text{ meV}$) in GaN among the most common acceptor species (Mg, Zn, Cd, C...). However, beyond a given Be-concentration, a deep PL band develops at 2.5 eV whose integrated intensity follows the Be-concentration measured by SIMS. This behavior strongly reduces the doping efficiency of Be. A consistent increase of the V_{Ga} density measured by Positron Anihilation Spectroscopy (PAS), concomitant with the Be increase (SIMS) and the deep PL band enhancement, is observed, in opposition to the Mg-doping case. The deep PL band is assumed to be generated by $V_{\text{Ga}}\text{-Be}_i$ complex defects, and a "family" of Yellow Luminescence bands is suggested, always including V_{Ga} together with a donor, either O, Si, or Be_i , with slight variations on the energy levels generated. A co-doping process with Be and Mg is proposed to enhance the Be efficiency as acceptor doping species.

Comparison of Si Doping in GaN MBE Grown by Plasma Nitrogen and Molecular Ammonia

Loren Pfeiffer

Abstract not available at time of publication.

P-Type Doping of GaN and Related Alloys

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The large acceptor binding energy in wide-band gap Nitrides imposes a fundamental upper limit of p-type conductivity, which can be obtained by conventional acceptor doping of homogeneous material. Therefore, two different alternative methods for achieving high p-type doping (and hence low series resistance) have been proposed, i.e. codoping with donors and acceptors to reduce the (isolated) ionized impurity scattering by Brandt et al. [1] and superlattice doping to enhance the electrical activation of acceptors by Schubert et al. [2]. We will briefly introduce the first concept, which uses either Be acceptor - O donor pairs or Be(Mg) acceptor-Si donor pairs. Due to the different site occupation of the respective donors, the specific complexes formed in the GaN crystal lattice will be different (for details see the presentation of Katayama-Yoshida et al.). Formation of the Be-O complex additionally increases the solubility limit of Be in GaN by at least two orders of magnitude. The replacement of isolated coulomb scatterers by dipole scatterers greatly enhances the mobility of heavily p-doped Nitrides.

However, above all concepts for novel p-type doping schemes of Nitrides, the minimization of the background impurity concentration deserves highest priority. We will define a few distinct sources for such unintentional impurity doping: (i) As contamination in MBE systems previously used for arsenide growth, (ii) impurities from improper substrate preparation (e.g. SiC), (iii) diffusion of constituent substrate species (atoms) into growing film (e.g. Si from Si substrate), and (iv) purity level of starting materials.

[1] O. Brandt, H. Yang, H. Kostial, and K.H. Ploog, Appl. Phys. Lett. 69, 2707 (1996)

[2] E.F. Schubert, W. Grieshaber, and I.D. Goepfert, Appl. Phys. Lett 69, 3737 (1996)

P- and N-type Doping of AlGa_N and GaN Films Grown by Metalorganic Chemical Vapor Deposition

Damien J. H. Lambert¹, Bryan S. Shelton¹, Mike M. Wong¹, Uttiya Chowdhury¹, Ho Ki Kwon¹, Ting Gang Zhu¹, Zuzanna Liliental-Weber², and Russell D. Dupuis¹

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We report the growth of high-quality *p*- and *n*-type doped AlGa_N and GaN films and AlGa_N/GaN heterojunction devices by low-pressure metalorganic chemical vapor deposition (MOCVD). The sources employed are adduct-purified trimethylgallium (TMGa), trimethylaluminum (TMAI), bis(cyclopentadienyl)magnesium (Cp₂Mg), silane (SiH₄), and ammonia (NH₃) precursors. The epitaxial structures are grown in an EMCORE D125 UTM reactor at pressures ~50-100 Torr. We have varied the growth conditions and have studied the correlation of the doping concentrations determined by C-V, Hall-effect, and secondary ion mass spectroscopy (SIMS), analyses with the growth conditions and the structural properties, e.g., the X-ray diffraction linewidths, surface morphology of the films.

In addition to *n*-type and *p*-type doped GaN and AlGa_N layers, various AlGa_N/GaN *p-n* heterojunction device structures were made to study the doping using I-V characteristics and C-V profiling. We show that Al_xGa_{1-x}N *x*~0.45 *p-i-n* diodes can be fabricated with *p*-type layers doped with Mg to $p \sim 7 \times 10^{17} \text{ cm}^{-3}$ as determined by C-V analysis. C-V analysis of *n*-type Al_xGa_{1-x}N *x*~0.45 layers indicates a concentration $n \sim 7 \times 10^{18} \text{ cm}^{-3}$. We will report on the characteristics of these layers and devices fabricated from such layers.

The Effect of Silicon Doping on the Structural and Electrical Properties of AlGa_N/Ga_N HEMT Structures

J.M. Redwing and K.K. Lew

Dept. of Material Science and Engineering, Penn State University, University Park, PA

D.A. Keogh, J.S. Flynn and E.L. Piner

Epitronics/ATMI, Phoenix, AZ

The AlGa_N/Ga_N heterostructure system has recently been the focus of extensive research as a promising new material for microwave power devices. Pseudomorphic AlGa_N layers on Ga_N produce a two-dimensional electron gas (2DEG) at the AlGa_N/Ga_N interface resulting in high sheet carrier densities and mobilities in nominally undoped material due to polarization effects. Further increases in sheet carrier density can be realized by modifying the HEMT structure to include intentionally doped layers in the AlGa_N barrier and/or the Ga_N channel.

We investigated the effects of intentional silicon doping on the structural and electrical properties of AlGa_N/Ga_N 2DEG heterostructures grown by MOVPE on SiC substrates. Identical 230Å Al_xGa_{1-x}N/Ga_N heterostructures were grown both undoped and with intentional Si doping in the top 200Å of the AlGa_N layer. The sheet carrier density increased as expected with intentional doping level within the range of Al compositions ($0.15 < x_{Al} < 0.37$) and doping levels ($1-5 \times 10^{18} \text{ cm}^{-3}$) investigated in this study. The room temperature electron mobilities of the Si doped samples, however, were found to be consistently lower than the undoped structures. Furthermore, the incorporation of Si was found to alter the surface morphology of the AlGa_N layers leading to reduced surface roughness compared to undoped heterostructures. The implications of our results on the design of AlGa_N/Ga_N HEMT structures will be discussed.

Structural Defect Characterization of ELO GaN Hydride VPE Layers

V. Wagner, O. Parillaud, H.J. Bühlmann, J.D. Ganière, and M. Illegems, Institut de Micro- et Optoélectronique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne EPFL, Switzerland

Hydride Vapor Phase Epitaxy (HVPE) in combination with Epitaxial Lateral Overgrowth (ELO) has shown to be very promising to obtain thick high quality GaN layers with low dislocation densities on sapphire. We have studied the influence of the carrier gas (hydrogen vs nitrogen), V/III ratios, stripe directions, and seed layer structures (crystalline vs. amorphous) on ELO growth and defect characteristics of GaN by HVPE. Growth was carried out on MOVPE-GaN/sapphire patterned with SiO₂ stripes, aligned along the $\langle 1 \ -1 \ 0 \ 0 \rangle$ and $\langle 2 \ -1 \ -1 \ 0 \rangle$ direction of GaN. The shapes of the stripes grown range from triangular \rightarrow trapezoidal \rightarrow rectangular \rightarrow inverse trapezoidal. Under certain conditions growth can be completely blocked on certain facets. Coalescence of triangular facets (grown using hydrogen/nitrogen as carrier gas) is preferred because dislocations that propagate vertically in the window region tend to bend by 90° when they reach these facets and continue then to propagate in the basal plane. In addition the formation of voids is prevented. TEM observations show these bend dislocations and a high density of horizontal defects above the mask. After coalescence, the surface is flattened in a second growth step under nitrogen. Cathodoluminescence images show clear differences between the window and mask region and regions grown using pure nitrogen and hydrogen/nitrogen mixtures. The luminescence intensity is significantly higher in the laterally grown regions. At the edge of the mask a blue shifted emission band from e-h-plasma recombination is observed indicating a high local free carrier concentration due to intrinsic defects or impurities.

Growth and Characterization of Bi-doped GaN Epilayers and GaN:Bi Lateral Epitaxial Overgrowth by Metal Organic Vapor Phase Epitaxy

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Many workers have studied the alteration of the surface structure and growth behavior by the addition of small amounts of dopants to a growth ambient. For example in the case of SiGe growth, antimony has been known to both segregate to the growth front and alter the surface energy of the SiGe. This change in surface energy results in an increase in the pseudomorphic thickness of the SiGe layer. Recently, a change in the ordering present in InGaP has been shown to be sensitive to the presence of surface adsorbates. In the present study, we have studied the role and effect of several isoelectronic centers introduced into the growth ambient on the structure and properties of GaN grown by metal-organic vapor phase epitaxy. Bismuth and other elements have been suggested as possible surfactants in the GaN system. A previous report has indicated some changes in the GaN:Bi microstructure using molecular beam epitaxy. In order to understand the impact of Bi on the growth process, we have studied the influence of Bi addition to the growth and properties of GaN epilayers on sapphire substrate and GaN:Bi lateral epitaxial overgrowth (LEO) by metal organic vapor phase epitaxy (MOVPE). The gas phase Bi concentration was varied by changing the trimethyl bismuth/trimethyl gallium mole fraction from 0, 0.5%, 0.8%, 2.5% to 4.5% while keeping other growth parameters as constant. The growth rate of GaN:Bi epilayers on sapphire was found to be independent on Bi doping concentration over the range investigated. A significant improvement on the crystalline quality of GaN:Bi epilayers was observed as indicated by a narrow line width in both symmetrical and asymmetrical rocking curves using double-crystal x-ray diffraction techniques. Low temperature photoluminescence of GaN:Bi showed additional emission peaks at 3.263eV and 3.179eV, which has been previously been attributed to the radiative recombination of an exciton bound to the Bi isoelectronic-hole trap¹. The surface morphology of highly-Bi-doped GaN epilayers was determined by atomic force microscopy (AFM). The surface at high Bi additions to the gas phase was characterized by a large number of surface depressions different from the more common dislocation-related surface pits often seen in MOVPE GaN. For GaN:Bi LEO growth, the lateral growth rate was increased and vertical growth rate was decreased at low Bi concentrations, while the lateral growth rate was reduced and vertical growth rate was enhanced at high Bi doping level. The role of the Bi in these strong changes in microstructure will be discussed as well as other isoelectronic impurities.

¹ W. M. Jadwisieniczak and H. J. Lozykowski, Mat. Res. Soc. Symp. Proc. 482 (1998) 1033.

Precision SiC epi Growth for Advanced FET Development

Michael S. Mazzola, Jeffrey B. Casady, Geoffrey Carter, Jana R. Bonds, John R. Ivy,
Michael C.D. Smith, Yaroslav Koshka, Thomas E. Schattner, and Stephen E. Sadow

Emerging Materials Research Laboratory (EMRL)
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The Emerging Materials Research Laboratory (EMRL) is exploring two advanced silicon carbide field effect transistor designs, one a JFET topology with the potential to operate as complementary logic, and the other a lateral power MOSFET topology for high-voltage high-impedance driver applications. Both devices have demanding requirements for precision epitaxial doping control.

For the JFET, epi layers with target doping levels in the low 10^{16} cm^{-3} and submicron epi thickness have been grown using a horizontal cold-wall atmospheric pressure CVD reactor. By appropriate configuration of the TMA injection point, the p^+ gate and n-type channel layers for the lateral JFET are grown consecutively during one continuous run without cross contamination of the n-type epi layer. Also, so-called TMA memory effects are avoided in the EMRL reactor during subsequent n-type growth runs.

For the lateral n-channel MOSFET topology, two different epi strategies are planned. The first uses a conventional p^- body layer on a p^+ 6H SiC substrate whose doping and thickness are critical to avoiding punch through to the substrate while managing the two-dimensional electrostatic field distribution under blocking conditions. Target net doping and thickness are mid 10^{15} cm^{-3} p-type and $10 \text{ }\mu\text{m}$, respectively. Intentional doping incorporation, rather than simply manipulating the background doping via site-competition epitaxy (i.e., silicon-to-carbon ratio control), is the preferred approach because the controlled introduction of aluminum or boron during growth should lead to more uniform, repeatable, and precision epi doping. Two methods are under investigation, including precision control of diluted gas-phase trimethylaluminum (TMA), and low vapor pressure doping from a solid boron-nitride source. Results from both methods have been obtained. For the diluted TMA process, p-type epi layers have been grown with net doping concentrations ranging from $5 \times 10^{15} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$. For the BN process, high-resistivity p-type epi layers have been grown with resistivities exceeding $10^3 \text{ }\Omega\text{-cm}$.

The second epi strategy for the MOSFET topology involves the growth of very high resistivity semi-insulating (SI) epi layers ($>10^9 \text{ }\Omega\text{-cm}$) using solid sources of transition metals, similar to the BN approach pioneered in EMRL. These epi layers are grown on n^+ 6H SiC substrates to produce a homoepitaxial equivalent to silicon-on-insulator technology. A p^- body layer is then grown on the SI/ n^+ epi-wafer followed by n-type implants, oxide growth, and metalization to complete the MOSFET. It will be shown that a significant reduction in body layer thickness can be achieved by operating in punch through on a semi-insulating epi layer.

The authors acknowledge Dr. David Larkin of the NASA Glenn Research Center, for helpful discussions on TMA doping technology. This work is supported by ONR grants N00014-99-1-1103 and N00014-98-1-0824 and monitored by Dr. Colin Wood.

Acceptor Dopants in III-Nitrides

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The dynamics of standard methods of p-type doping will be discussed. The role of substrate temperature, V/III ratio, and substrate polarity will be discussed. Never before reported anomalies such as a drastic decrease in incorporation rate at low substrate temperatures will be discussed as well as the quantification of concentration dependant diffusivities/surface segregation effects. The transient behavior of Mg incorporation will be demonstrated. Guidelines for maximum p-type dopant incorporation will be given and the effects and causes of dopant concentration dependence on electrical activity will be discussed.

A novel, growth method will be discussed that may result in increased activation of high concentrations of p-type dopants. This approach is based on the external control of the fermi-level position during growth. By controlling the fermi-level during growth, the formation energy for detrimental compensating defects can be enhanced, resulting in less compensation. The approach will be discussed on a theoretical level as well as efforts and limitations to practically implement the approach.

Control of Valence States of ZnO and AlN by Codoping Method

Tetsuya YAMAMOTO and Hiroshi KATAYAMA-YOSHIDA*

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Our recent works present a large contribution to the materials design for obtaining low-resistivity *p*-type wide-band-gap semiconductors such as GaN[1], AlN, ZnO and ZnS.

We have investigated the electronic structures of *p*- or *n*-type doped ZnO based on *ab initio* electronic band structure calculations. We find *unipolarity* in ZnO; *p*-type doping using Li or N increases the Madelung energy while *n*-type doping using Al, Ga, In or F species decreases the Madelung energy. We find a very weak repulsive interaction between Li acceptors in Li-doped ZnO with a remarkable increase in the Madelung energy, in contrast with the case of N-doped ZnO. Codoping using reactive codopants, Al and Ga, enhances the incorporation of N acceptors in *p*-type codoped ZnO. We find the delocalized states of N for *p*-type ZnO codoped with 2N and Al or Ga[2]. Very recently our prediction of materials design for the fabrication of low-resistivity *p*-type ZnO by the codoping method using N species as acceptors and Al or Ga as codopant donors was verified by a successful experiment conducted by Osaka Group [3]. For ZnO:(2Li and F), total energy calculations show that the formation of the complex with $\text{Li}_{\text{Zn}}\text{-F}_{\text{O}}\text{-Li}_{\text{Zn}}$ which occupy nearest neighbor sites is energetically favorable with a decrease in the Madelung energy, which produces low-resistivity *p*-type ZnO crystals.

We have investigated the electronic structures of *n*-type O-doped and *p*-type C-doped AlN crystals with wurtzite structures based on *ab initio* electronic band structure calculations. We find the strongly localized impurity states for *p*-type C-doped AlN compared with that for *n*-type O-doped AlN. For the materials design to fabricate low-resistivity *p*-type C-doped AlN, we study the effects of oxygen incorporation on *p*-type C-doped AlN. We verify the delocalization of the impurity states for *p*-type AlN:(2C and O) with a decrease in the Madelung energy [4].

We also discuss the effects of codoping using group III elements on ZnS doped with N species and the experiments.

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Magnesium and Beryllium Doping During rf-plasma MBE Growth of GaN

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While magnesium is currently the most technologically important p-type dopant for GaN, Be also shows promise. Although Mg has been extensively studied in the last several years, incorporation mechanisms during growth by molecular beam epitaxy (MBE) remain unclear. For example, previous studies have presented results that indicate Mg incorporation is independent of Mg flux over a wide flux range but is quite sensitive to substrate temperature, [1] and there is evidence for significant surface accumulation of Mg. [2] Two competing models have been put forth to explain much of the observed behavior. The first assumes the presence of a surface accumulation layer, with dopant incorporation linked to surface accumulation with incorporation driven by segregation effects. The second model assumes the presence of a finite concentration of sites on the growing surface where the Mg is strongly incorporated.

We present the results of a study of both Mg and Be incorporation for both N- and Ga-polarity oriented GaN that strongly indicate surface accumulation occurs for both dopants under Ga-rich growth conditions. Indeed, many of the doping profiles we obtained strongly resemble classic cases of Sn segregation in GaAs or Sb segregation in Si growth. Figure 1 shows such a doping profile for Be incorporation. The exposure times of the growing surface to Be through shuttering is shown schematically in the figure. In addition, we observe a significant difference in Mg incorporation between the two polarities, with Mg incorporating at a rate up to 20 times higher for Ga-polarity surfaces. There is less of an effect for Be, with a larger incorporation on the N-polarity. The phenomenon of polarity inversion linked to Mg on the growing surface was observed, and dramatically illustrates the lower incorporation rate that occurs for the N-polarity surface. An additional result of significance is that the presence of atomic hydrogen significantly alters the incorporation kinetics of both Mg and Be, decreasing segregation effects while maintaining or increasing the actual incorporation rate.

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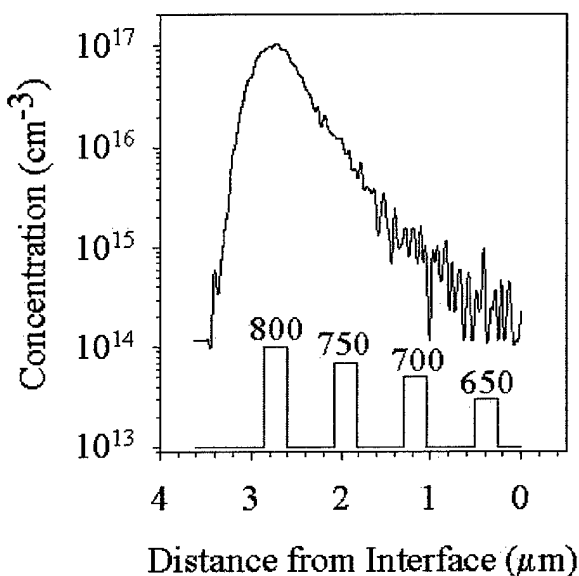


Figure 1. Be incorporation into Ga-polarity GaN grown by rf plasma MBE at 675°C for various Be oven temperatures, which are indicated schematically along with length of exposure to the Be flux.

Donor and Acceptors in Undoped and Si-doped Heteroepitaxial GaN Layers

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During the last decade remarkable progress has been made in the areas of III-nitride material science and device technology. Presently, progress on increasing device yield seems to be strongly limited by material quality. The high deposition temperature usually required for heteroepitaxial growth of these wide bandgap materials increases fundamental material problems such as residual strain, thermal expansion coefficient, low energy defect formation, and impurity incorporation. Doping incorporation, activation and self-compensation are difficult to control at high temperatures. Full realization of the electronic and opto-electronic applications of III-nitrides requires an understanding of the role of incorporation and activation of unintentional and doped impurities, as well as extended defects.

To investigate the incorporation and activation of impurity and extended defects in GaN films deposited on sapphire, we have performed photoluminescence studies on a set of undoped and Si-doped GaN layers deposited at different growth pressures. The GaN layers were grown on AlN nucleation layers deposited under identical conditions, and used the same SiH_4 dopant flow, V/III ratio and total flows in a close-spaced showerhead reactor. The growth pressure was adjusted after the growth of the nucleation layer, prior to ramping up to the epitaxial growth temperature. TEM studies indicate that the film grain size increases with increasing growth pressure (1). Transport measurements carried out on undoped and Si-doped films shown that: a) undoped films deposited in the pressure range between ~40torr to ~130torr have high breakdown voltages, which decrease with increasing growth pressure until the films become conductive; b) Si-doped films are conductive, but the carrier concentration and mobility increase with increasing growth pressure.

Photoluminescence (PL) measurements carried out in undoped and Si-doped samples show emission bands associated with recombination processes involving free-excitons (FE), excitons bound to neutron donors ($\text{D}^0\text{-X}$), a donor-acceptor pairs (DAP with no-phonon line at 3.26eV), yellow band, and a band at 3.05eV. The latter, in general observed in films with high breakdown voltage, may be partially responsible for the compensation of unintentional and doped donor impurities (2). An intense $\text{Si}^0\text{-X}$ PL-band and multiple phonon replicas dominate the PL spectrum of Si-doped samples grown at 130torr. The 130torr sample also has a high carrier concentration and exhibited the highest room temperature carrier mobility for this set of samples. These together suggest a low level of compensation and scattering. Si-doped samples grown at pressures higher than ~130torr shown a DAP which is associated with a shallow acceptor (3). This observation is surprising since the samples have not been intentionally doped with acceptors. Discussion about the origin of these recombination processes and supporting SIMS data will be presented.

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Influence of Multiple-Step Annealing on P-type Conductivity and Contact Behavior

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In galliumnitride (GaN) technology, rapid thermal annealing (RTA) is a well established method to achieve p-type conductivity and improve contact resistances. However, almost all reported processes contain only single temperature steady-states and the thermal budget, often defined as temperature times process duration, is rather high. By using two- or multiple-step processes, the thermal budget can be reduced significantly. We report on the use of multi-step annealing procedures employing ultra fast RTA systems capable of temperature gradients of 20 – 50 °C/s.

The two-step processes for p-type activation consist of a low temperature annealing at temperatures between 350 °C and 700 °C and a short-time high temperature step. As well for a 10 min single-step process at 800 °C as for a two-step process with a 5 min annealing step at 600 °C and a 30 s diffusion step at 950 °C p-type conductivity of 0.55 1/ cm is achieved, but only half of the thermal budget is required for the second process.

For contacts the process consists of a "diffusion" step, where the contact metal diffuses into GaN to build an intermediate semiconductor layer (ISL), and a subsequent alloying step performed at temperatures above the eutectical point of the contact metals. The treated contacts are examined regarding to IV-behavior and specific contact resistances, determined from transmission line method (TLM) measurements. Investigations are made with Ni/Au and Ni/Pd/Au metallization schemes for p-contacts and Ti/Au as n-contacts.

P-doping of III-Nitrides

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P-doping of GaN and InN has been attempted using Mg, C and Be as dopants. While C and Be can compensate n-type material, only Mg has been shown to produce free holes in GaN. In addition to acceptor depth, Mg is difficult to employ because of low sticking coefficient. While doping near interfaces of AlGaIn/GaN can produce low ionization energies, high substrate temperature growths can result in n-type conductivity by polarization induced charge rather than p-type. This is because Mg sticks so poorly at high substrate temperatures. Memory effects have also been seen from using Mg doping at high flux densities.

At very high Mg fluxes, Mg doping of InN results in n-type conductivity. Lower Mg fluxes will be attempted prior to this meeting. The lower temperature InN growths (400°C-500°C) presumably do not suffer from Mg sticking problems. Undoped InN has been grown with high resistivity at lower substrate temperatures, but it is usually n-type in the ranges of better InN quality where Mg doping has been attempted thus far.

Doping of GaN with Mg, Ca, and C during MOVPE

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Highly conducting p-type layers are of critical importance for optoelectronic devices. Despite its intrinsic limitation (deep character of the acceptor, formation of Mg-complexes, poor hole mobility), Mg is currently the most suitable p- doping element for GaN and AlGaIn alloys. However, its incorporation in GaN by MOVPE raises several difficulties: premature reaction of the Mg precursor with ammonia, incorporation of Mg-H complexes which should be destroyed in a post-growth annealing, incorporation of deep states responsible for the blue luminescence as well as compensating species, incorporation of extended defects (antiphase boundaries).

The search for better or more appropriate p doping impurities is limited in MOVPE to Ca, and C (Be can not be safely used in MOVPE, group II impurities like Zn and Cd, with d-electrons introduce deep states). According to theoretical estimation, Ca is not expected to bring significant improvements compared to Mg, however implanted Ca behaves like Mg in GaN and we tried to implement Ca doping in MOVPE using pentamethyl-biscyclopentadienyl calcium ($(\text{Me}_5\text{Cp})_2\text{Ca}$) as precursor. It was expected with methyl substitution to get high enough vapor pressure. However, the Ca incorporation in MOVPE was too low for p doping.

Because of its expected lowest binding energy in GaN among acceptors, C is *a priori* an attractive species for p doping. Although the solubility of C in GaN is assumed to be low, C doping was achieved in MBE. In MOVPE, CCl_4 was widely used as precursor for p doping of GaAs in MOVPE. In the present study, CCl_4 was introduced in the gas during the epitaxial growth of GaN on sapphire. Whatever the partial pressure of CCl_4 the GaN remain n-type although low temperature photoluminescence spectra exhibit well defined DA recombination peaks (with LO replica) at 3.27 eV. SIMS analysis reveals that C is indeed incorporated up to 10^{19}cm^{-3} , however in addition to C, Si and O are introduced at densities much above the usual residual n-level. It may occur that HCl produced at high temperature in the growth chamber react with the quartz walls. To get rid of these limitations, propane C_3H_8 was used as precursor. PL data reveal DA peaks most likely related to C, however SIMS analysis showed that C is non-uniformly incorporated.

In conclusion, in MOVPE, Mg remains the most suitable and most efficient p-doping impurity even though its use in MOVPE requires post-growth activation.

New Insights in P-type Doping of III-Nitrides

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Improvements in *p*-type doping of III-V nitrides are still necessary to achieve superior device performance of nitride-based devices. The achievable hole concentrations in *p*-type GaN are limited, and the *p*-type conductivity decreases in AlGaN alloys. A comprehensive understanding of the behavior of point defects and extrinsic impurities in nitrides is essential for improving doping. Acceptor impurities need to exhibit adequate solubility and modest ionization energy, and compensation needs to be suppressed. Such compensation may be due to native point defects that are spontaneously formed during growth; to incorporation of the dopant impurities in undesired configurations; or to unintentional incorporation of impurities. We have addressed these issues with the aid of first-principles computations, based on density-functional theory and *ab initio* pseudopotentials.

Magnesium has emerged as the dopant of choice, but achievable hole concentrations are still limited due to the solubility of Mg, as well as to partial compensation by nitrogen vacancies. Our comprehensive investigation of alternative acceptors showed that only beryllium is promising. We find a tendency for neutral Be to move off the substitutional site; this does not affect the ionization energy, however. We also find a much larger binding energy for Be-H complexes than previously found for Mg-H. The biggest problem with Be is that, in the bulk, Be interstitial donors are energetically as favorable as Be_{Ga} acceptors. We have therefore performed calculations to study Be interstitials in detail. Calculations for Be near the GaN(0001) surface indicate that Be atoms in an interstitial site just below the surface are unstable with respect to Be atoms on substitutional sites. This will tend to suppress formation of Be interstitials. Still, it is essential to assess the diffusivity of Be interstitials, in order to establish whether they can migrate during the growth or be moved out of the sample by thermal annealing after growth. We have mapped out migration paths for Be, both in zinc-blende and wurtzite GaN. The migration barriers are fairly high, and we will discuss the conditions under which motion of Be interstitials can be expected.

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Acceptor Activation in Ga (Al)N and the Effect of Dislocations on Electronic Transport in GaN

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All acceptor impurity atoms in Ga (Al)N have been shown to have very low ($\sim 10^{-2}$) activation. A straight forward hydrogenic model for the ionization energy clearly shows this, especially if the correct value for the relative dielectric constant is used. When the acceptor binding energy exceeds the transverse optical phonon energy of $\sim .09$ eV, the high frequency relative dielectric constant of 5.4 must be used ⁽¹⁾, yielding $\sim .30$ eV for the predicted ionization energy. At low frequencies, the motion of the light, charged Nitrogen atom yields a substantially higher value (8.9) of the relative dielectric constant. Even if the low-frequency relative dielectric constant is used, the ionization energy predicted is greater than the transverse optical phonon energy. Thus it is clear that the high frequency relative dielectric constant is the correct value to use in this calculation. The related orbit diameter for the acceptor energy is ~ 10 Å. Threading dislocations are electrically active as a line of very deep (~ 1.2 eV) acceptor states (with line density $\sim 2 \times 10^7/\text{cm}$) that partially fill and deplete donors nearby ⁽²⁾. These states are optically active, with ~ 2.2 eV transitions from the conduction band, whenever the dislocation states are not filled. The dislocations have a reduced barrier for electrons at the surface, where electrons may be injected into or removed from these states. Electron mobility perpendicular to the dislocations is reduced by scattering from the charged dislocation line⁽²⁾.

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Study of Magnetic Resonance (ODMR) and Optical Properties of Shallow Acceptors in GaN

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Be and Mg are the shallow acceptors that are the most promising ones for p-doping purposes in III-N device structures. Detailed information on the physical properties of these acceptors in GaN is still not available. We present new data from magnetic resonance at microwave frequencies of both 35 GHz and 95GHz, which map out the g-factor of both acceptors, and its anisotropy, relevant for the description of these acceptors in the effective mass model. The data are compared with optical data (photoluminescence), which give information on the hole-phonon coupling. In particular for Mg a correlation between the behavior of the g-factor and the phonon coupling is observed, and will be discussed.

Investigation of Dopants in GaN by Ion Implantation and Optical Spectroscopy

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Ion implantation is a useful method to survey the properties of various dopants in GaN and investigate their activation without performing difficult doping experiments during the crystal growth process. Precisely known quantities of the desired impurities can be introduced into high purity starting material without the likelihood of undesired species being introduced. Using low temperature photoluminescence (PL), the levels introduced by the implanted species can be studied spectroscopically, which can yield valuable information even if full electrical activation is not achieved. We have used this method to study Mg, C, and Be dopants in GaN, and have also investigated Zn-doped HVPE material. The starting material consisted of high quality undoped heteroepitaxial HVPE and MOCVD layers with sharp exciton linewidths (e.g., 1.8 meV FWHM) and extremely weak acceptor-related or deep level features. Implantations were designed to produce the same flat profile for each species with low concentrations of 1×10^{15} , 1×10^{16} , or $1 \times 10^{17} \text{ cm}^{-3}$, in order to yield high quality optical spectra. Co-implantations of Ne, Al, P, or Ar at a dose of $1 \times 10^{17} \text{ cm}^{-3}$ are also being performed to test the effect of additional damage and/or perturbations of the stoichiometry on the optical activation behavior. The implanted samples are annealed for 10 s in N_2 at 1300 °C using a reactively sputtered AlON cap to prevent N loss. Control samples with damage implants only or no implants are used to test the effectiveness of the annealing procedure and identify effects uniquely associated with the implanted species. Only a slight broadening and no new spectral features are caused by the annealing process alone. The Mg implants yield clear evidence of optical activation of the Mg acceptor level, including a sharp (2.8 meV FWHM) neutral acceptor-bound exciton (A^0X) with a 12.2 meV localization energy; a strong donor-acceptor pair (D^0-A^0) peak at 3.270 eV, and a conduction band-to-acceptor peak at higher temperatures around 3.284 eV (50 K). The latter yields an acceptor binding energy of 224 meV. A new broad peak appears at 2.35 eV at an annealing temperature of only 800 °C, but is largely suppressed in favor of the higher energy peaks at higher annealing temperatures. Co-implantation of Ar with Mg apparently improves its activation, yielding a 4-5 \times stronger (D^0-A^0) peak relative to the residual donor-bound exciton peak present in the starting material. Co-implantation of P with Mg produces a new, deeper peak at 3.248 eV which is apparently a (D^0-A^0) band, together with phonon replicas and the usual 3.270 eV peak. Implanting P alone produces only an isoelectronic bound exciton no-phonon line at 3.196 eV, together with a highly structured phonon sideband peaking at around 2.95 eV. Implants of Be and C do *not* produce strong acceptor peaks, in dramatic contrast to the Mg case. No (A^0X) peak is observed and the (D^0-A^0) peak is at least 50 \times weaker than in the Mg case. A strong enhancement in the yellow PL band at 2.2 eV is observed for *both* Be and C, suggesting it may be damage-related. Co-implants of Ne or Ar do not produce clear optical activation in the Be case; study of co-implants with C is in progress. Measurements of Zn-doped HVPE material confirm the existence of a Zn (A^0X) peak with a localization energy of 24.5 meV. A broad (D^0-A^0) structure peaking at 2.92 eV is observed, and its no-phonon peak is clearly resolved for the first time at about 3.10 eV. This peak yields a Zn acceptor binding energy of about 400 meV.

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Doping Limitations in Wide-Gap Semiconductors

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The "doping" problem in semiconductors will be discussed in terms of the Amphoteric Defect Model (ADM). Over than 10 years ago¹ it has been shown that the formation energy as well as the nature (donor- or acceptor-like) of vacancy like defects depends on the location of the Fermi energy with respect to a common energy reference, the Fermi level stabilization energy (E_{FS}). Experiments with heavily damaged semiconductors have shown that in all semiconductors E_{FS} is located at energy of about 4.9 eV below the vacuum level. Doping of semiconductors with donors (acceptors) shifts the Fermi energy upward (downward) resulting in an increased incorporation of compensating acceptor-like (donor-like) defects. This effect limits the range of possible Fermi energies and thus also the maximum free electron (hole) concentration that can be achieved by doping under thermodynamic equilibrium conditions. The maximum (minimum) Fermi energy is located approximately at $E_{FS}+0.9$ eV ($E_{FS}-0.8$ eV) and is the same for all III-V compounds. For more ionic II-VI compounds a wider range of Fermi energies from $E_{FS}-1.3$ eV to $E_{FS}+1.3$ eV is found.² It has been shown most recently that the ADM accounts very well for the observed trends in maximum doping achievable for a large variety of semiconductor material systems including semiconductor compounds as complex as group I-III-VI₂ ternaries.³

In general semiconductors with the conduction (valence) band located close E_{FS} can be doped heavily n-type (p-type). In several extreme cases of wide gap semiconductors a certain type of doping cannot be realized at all. For example ZnTe or diamond with their valence bands located close to E_{FS} can be very easily doped with acceptors. However, because the conduction band of these materials is removed so far from E_{FS} n-type doping is difficult if not impossible to achieve. On the other hand CdSe, ZnO or even CdF₂ with their conduction bands located very close to E_{FS} are excellent n-type conductors but cannot be doped p-type. The n-type (p-type) doping efficiency can be improved by shifting the conduction (valence) band towards E_{FS} . An interesting example of this effect is the recent discovery that GaNAs alloys with small (few percent) nitrogen content can be doped heavily n-type.⁴ The origin of this effect can be traced directly to the very large N-induced downward shift of the conduction band edge in these alloys.⁵

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Hall-Effect Characterization of Mg-Doped GaN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x \leq 0.17$)

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The accomplishment of reliable p-type doping for GaN and AlGa_N device layers was a critical cornerstone for the fabrication of high-efficiency light emitting and laser diodes based on III-V nitride materials. Today, room-temperature hole concentrations in the range between 5×10^{17} and $1 \times 10^{18} \text{ cm}^{-3}$ are routinely achieved enabling high flux light emitting diodes with high quantum efficiency and low drive voltages. However, the exact position of the Mg level in the bandgap of Mg-doped GaN and AlGa_N has not been established.

From variable temperature Hall-effect measurements, it has been shown that Mg doping of GaN leads to the formation of acceptors with activation energies in the range between 130 and 180 meV depending on acceptor concentration and the concentration of compensating donors. As a consequence of the depth of the acceptor level, Mg is incorporated in concentrations $> 10^{19} \text{ cm}^{-3}$ to achieve hole concentrations of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. It is expected that the Mg acceptor level moves deeper into the band gap for AlGa_N with increasing AlN composition further reducing the ionization efficiency of Mg-acceptors.

We have employed variable-temperature Hall-effect measurements in the temperature range between 70 and 730 K to study the electronic properties of Mg acceptors in GaN and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x \leq 0.17$). For the analysis of the temperature dependence of the hole concentration, the interaction between ionized acceptors was taken into account. These interactions lead to a lowering of the effective activation energy at high acceptor concentrations. The activation energy for ionization of Mg acceptors for GaN was determined to be $(208 \pm 8) \text{ meV}$. This activation energy is independent of the acceptor concentration and is expected to quantitatively agree with the true ionization energy of Mg acceptors in GaN. The Mg concentration in our Mg-doped GaN samples was determined by Secondary Ion Mass Spectrometry and was found, in general, to agree with the acceptor concentration as determined from the analysis of the Hall-effect data.

For the Mg-doped AlGa_N samples the activation energy for ionization of Mg acceptors was found to increase by $\sim 3.2 \text{ meV}$ for 1 % increase of the AlN composition. For an AlN composition of ~ 17 %, the highest AlN composition investigated in this study, the activation energy is $\sim 260 \text{ meV}$. Only ~ 0.1 % of Mg acceptors are ionized at room temperature for $\text{Al}_{0.17}\text{Ga}_{0.83}\text{N:Mg}$.

Native Point Defects in ZnO Substrates: Electrical and Optical Properties

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Wurtzitic ZnO is a wide bandgap (3.437 eV at 2K) semiconductor which has many applications, such as piezoelectric transducers, varistors, phosphors and transparent conducting films. Most of these applications require only polycrystalline material; however, recent successes in producing large-area single crystals have opened up the possibility of producing blue and UV light emitters, and high-temperature, high-power transistors. The main advantages of ZnO as a light emitter are its large exciton binding energy (60 meV), and the existence of well-developed bulk and epitaxial growth processes; for electronic applications, its attractiveness lies in having high breakdown strength and high saturation velocity. Optical UV lasing, at both low and high temperatures, has already been demonstrated, although efficient electrically-pumped lasing must await the further development of good p-type material. ZnO is also much more resistant to radiation damage than are the other common semiconducting materials, such as Si, GaAs, CdS and even GaN; thus it should be useful for space applications. In spite of the short time span associated with recent ZnO development, at least one photonic device has already shown outstanding characteristics. A MSM ultraviolet photodetector, fabricated on MOCVD-grown ZnO, shows a low frequency photo-responsivity of 400 A/W, with a sharp cut-off at a wavelength of 373 nm [1]. Also Schottky photodetectors have been fabricated with this same material. In summary, the future is bright for ZnO photonic devices, and it is also likely that electronic devices will soon be developed for high-power, high-temperature applications. (The latest advances in ZnO materials and devices are included in Ref. 2.).

Present-day, commercially available, 2-inch ZnO wafers are of very high quality. The ZnO crystals employed in the present study were grown by Eagle-Picher, Inc., and had 300-K and peak Hall mobilities of approx. 225 and 2000 cm²/V-sec, respectively, and photoluminescence (PL) donor-bound-exciton linewidths of < 0.3 meV. Temperature-dependent Hall-effect (TDH) analysis revealed two donors, with approx. energies of 30 and 60 meV, and concentrations of 1×10^{16} and 1×10^{17} /cm³, respectively, and an acceptor concentration of 2×10^{15} /cm³ [3]. Epitaxial ZnO layers are still grown mainly on less expensive substrates, such as sapphire, and thus have somewhat degraded electrical and optical properties. For example, ZnO grown by plasma assisted MBE on sapphire has a 300-K mobility of approx 100 cm²/ V-sec, and a DBE linewidth of approx 3 meV [4].

It has long been assumed that the electrical and optical properties of ZnO are controlled by native point defects, in particular, the O vacancy VO and/or the Zn interstitial Zn I . However, very few controlled experiments have tested this important hypothesis. With the recent availability of large, high-quality, single-crystals of ZnO, it is now possible to use high- energy electron beam irradiation to create (through lattice atom displacements) relatively small concentrations of isolated point defects and observe their effects on the electrical and optical properties of these crystals. The conclusions so far are the following:

1. For c-axis irradiation, electrons directed at the Zn face of n-type material produce damage at a higher rate than those directed at the O face. Also, it appears that simple, nearest neighbor Frenkel pairs (such as VZn - ZnI) are not stable, because the positively- charged Zn I will immediately recombine with the negatively -charged VZn. In fact, stability is found only in larger, "chain-like" defects, such as VZn - Zn O - OZn --- Zn I, especially if the Zn I has sufficient kinetic energy to drift away from the rest of the complex. The defect-donor energy is about 30 meV, which is the same as that usually observed in the as-grown material; thus, it is probable that the dominant native donor is a Zn I - related defect, rather than one involving VO. The defects anneal out at about 325 C, well described by a first-order process with an activation energy of 1.73 eV.

Cole Litton and David Look: Abstract (Con't)

2. The production of the chain defect mentioned above requires a high electron energy, at least 1.6 MeV. Thus, ZnO is more "radiation hard" than some of its counterparts, such as Si, GaAs, and even GaN, and might be useful in high-radiation environments, such as those encountered in space.
3. Electron irradiation also affects the photoluminescence (PL) intensity less in ZnO than in those other semiconductor materials. For example, the overall PL intensity decreases by less than a factor of two after a 1.6 MeV, 4×10^{16} /cm² irradiation. This fact suggests that non-radiative centers are not easily formed, and thus, that photonic applications will also fare well in high-radiation environments.

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Compensation Mechanisms in P-type GaN

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The stability of defects present in GaN:Mg has been investigated using photoluminescence (PL) spectroscopy. The two dominant defect-related PL emission bands in p-type GaN were studied, the blue band at 2.8 eV and the ultraviolet (UV) emission band at 3.27 eV. The intensity of the 3.27 eV PL band increases with increasing resistivity, whereas the 2.8 eV PL band intensity increases with a decrease in resistivity. The luminescence data is explained by a model whereby the concentration of luminescent centers depends on the Fermi level position. For a Fermi level of $E_v + 0.6$ eV, there is a cross-over in the stability of the specific donor defects responsible for the 3.27 eV and the 2.8 eV luminescence, respectively. The shallow donor responsible for the UV band is attributed to hydrogen, whereas the deep donor defect responsible for the 2.8 eV band is attributed to a nitrogen vacancy complex. Experiments on the photoluminescent properties of GaN:Mg co-doped with donors will also be presented.

Electrical and Optical Characterization of Dopants in Group-III-Nitrides Under High Pressure

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There are three very important areas of the high pressure application in Group-III-Nitride research and technology. They consist of i) growth of bulk (undoped and doped) GaN crystals under nitrogen pressure of 1.5-2 GPa; ii) identification of the character of electrically and optically active dopants and defects; iii) high temperature annealing of nitrides (e.g. after ion implantation), under 1-1.5 GPa of nitrogen pressure which enables to increase the decomposition temperature of GaN from about 1000°C to 1600°C.

In this talk we concentrate on the first two aspects of the high pressure use. In particular on properties of high pressure grown GaN bulk crystals doped with Mg and Be. Modification of optical and electrical characteristics of GaN crystals as a function of the dopants concentration will be presented. Moreover, effects of hydrogenation of bulk GaN:Mg and GaN:Be will be discussed.

In the second part of the talk results of pressure studies aiming determination of the mechanism of the radiative recombination in Mg doped GaN will be given. Comparison between lightly (luminescence at 3.27 eV followed by phonon replicas) and highly Mg (blue luminescence) doped bulk crystals and GaN/Al₂O₃ will be given. Though, the both emission processes consist of donor-acceptor-pair recombination, in the case of light doping, the shallow donor and shallow acceptor are responsible for the radiative recombination. In contrast, for blue luminescence (2.8-3.1 eV) a deep donor becomes the initial state determining radiative recombination processes. This deep donor appears as a center compensating Mg acceptors in highly Mg doped bulk GaN as well as heteroepitaxial layers of this semiconductor.

Shallow Acceptors in III-Nitrides

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We have shown that if donors and acceptors bind to each other more strongly than the binding energy of the host atoms, the donor and acceptor levels will move out of the bandgap into the conduction band and valence band, respectively. This was verified by electrical and spectroscopic measurements.^[1]

An extension of this interatomic interaction suggests the possibility of combining three elements that together may result in a net shallower acceptor in GaN.

We will be pleased to acknowledge financial support for this work if and when such support materializes.

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P-type and N-type Polarization Doping in GaN-based Heterostructures

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We present the results of the band structure calculations for a gated AlGaIn/GaN heterostructures. The spontaneous and piezoelectric polarizations, as well as strain relaxation were taken into account. The results confirm that polarization charge can induce up to $5 \times 10^{13} \text{ cm}^{-2}$ holes at the AlGaIn/GaN heterointerface. Depending on hole mobility, we show that the 2D hole gas can be achieved for hole sheet densities on the order of 10^{13} cm^{-2} or higher. For smaller densities, 3D hole accumulation layer can exist. The results suggest that a piezoelectrically induced 2D-hole gas can be used for the reduction of the base spreading resistance in AlGaIn/GaN-based Heterostructure Bipolar Transistors. We compare these results with predicted dependencies of the polarization n-type in heterostructures. We also report on the simulation of an Induced Base Transistor (IBT) based on n-type GaN-AlGaIn-GaN-InAlGaIn heterostructure with a thin AlGaIn emitter barrier and a thin GaN quantum well base. Our simulations show that such a majority carrier device should have a high collector current density, a low base resistance, a high current gain, and is expected to be a viable competitor to GaN-based Heterostructure Bipolar Junction Transistors.

Polarization Induced Effects in P-doped $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlGaN/GaN Heterostructures

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In the past few years, much experimental and theoretical effort has been directed towards the fabrication and understanding of polarization induced two-dimensional electron gases in hexagonal AlGaN/GaN heterostructures for high power microwave devices. Most of the investigations have concentrated on the properties of n-type heterostructures as it was commonly believed that the difficulty of growing p-type nitride films combined with the large binding energy of Mg acceptors would make it very difficult to grow and process AlGaN/GaN based devices with a significant hole conductivity. Recently it was shown that piezoelectric fields can be used to lower the ionization energy of Mg acceptors in AlGaN/GaN superlattices grown by metalorganic chemical vapor deposition (MOCVD).

We have deposited Mg doped AlGaN/GaN based heterostructures with N- and Ga-face polarity on c- Al_2O_3 substrates by plasma induced molecular beam epitaxy (PIMBE) in order to realize hole accumulations with high sheet carrier concentrations close to AlGaN/GaN interfaces. C-V profiling and Hall effect measurements were carried out to determine the sheet carrier concentrations and their dependence on the alloy composition of the barrier. The role of polarity on the carrier distribution was measured and compared to theoretical simulations, taking into account electric fields caused by piezoelectric and spontaneous polarization. For this purpose self consistent solutions of the Poisson and Schrödinger equations were obtained for heterostructures with different alloy compositions of the barrier. We have determined the best design to lower the ionization energy of Mg acceptors and to enhance the transfer of holes into the GaN channel. For accurate calculations it was necessary to find a detailed description of the electronic structure of Mg doped GaN/AlGaN/GaN based heterostructures taking into account the electric subbands of the valence band. The activation energy of Mg acceptors needed for the simulation were measured for epitaxial AlGaN layers with Al-concentrations of up to 30%.

The theoretical predictions as well as the experimental results of the electronic transport properties of p-type AlGaN/GaN heterostructures will be presented.

The Influence of Polarization Effects on Impurity Incorporation in Nitride Materials

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It is now well established that the strong spontaneous polarization and piezoelectric effects in nitride materials can give rise to large induced charge densities at surfaces and interfaces of nitride heterostructures. It can be expected that there are also additional, secondary effects of the polarization fields on doping, since the polarization-induced charges and potentials can change the rate of incorporation of impurities present during crystal growth. This paper provides insight into the magnitude and scope of such effects.

Polarization fields influence dopant incorporation through their effect on surface potential and electric field. The discontinuity in polarization at the semiconductor surface gives rise to a bound charge at the crystal surface, of the order of 2×10^{13} electron charges per cm^2 (approximately 10^{-2} charges per lattice site). This charge, in turn, is compensated by charges residing in surface states, in a depletion region near the semiconductor surface, or by charges associated with species adsorbed on the surface. The fermi level at the semiconductor surface will not be precisely pinned relative to the band edges, as long as the density of surface states is not excessively large. Thus the near surface band-bending will change as a result of the polarization charge. The change in fermi level at the surface relative to the band edges directly influences the formation energy of various species within the surface layers of the growing crystal, and thus changes their equilibrium concentrations relative to surface or gas phase species.

For the growth of GaN on the Ga-face, the spontaneous polarization produces a negative (acceptor-like) induced charge at the surface. Measurements have shown, moreover, that the growing crystal is frequently under stress. This produces a piezoelectric component of polarization that modifies the surface charge. Growth of AlGaIn or InGaIn heterostructures changes the polarization surface charge further, in a manner that depends on the thickness of the grown layer and the degree of lattice relaxation with respect to the substrate. Defects, such as V-grooves and dislocations, have stress fields and geometries that also modulate the polarization charge.

An acceptor-like surface charge will enhance the incorporation of defects with positive charge. Ionized donors (such as silicon, oxygen or nitrogen vacancies) will experience higher incorporation, as will hydrogen (as H^+). The enhanced impurity incorporation at the surface may not persist as the crystal growth front advances, however. Limiting behaviors are: a) rapid redistribution, so that the impurity is in thermal equilibrium throughout the material (then the changes in surface potential may not affect the bulk concentration); and b) the impurities may be completely immobile in the growing crystal, and thus become incorporated in the bulk in the same density as at the growing surface.

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Doping Studies of Quaternary AlGaInN Materials and AlGaInN/InGaN Heterostructures and Quantum Wells

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We report on experimental studies of n-type and p-type doping in AlGaInN/GaN materials system. Our results show that n-type doping of quantum wells allows us to partially screen the polarization fields and enhance the photoluminescence by making the quantum well more symmetrical and by increasing the overlap integral. The obtained results show that incorporation of Al and In into barriers results in a blue shift of the emission peak and a significant increase in emission intensity. The modulation doping of QWs results in a blue shift of PL peak and non-monotonous change of the emission intensity. The maximum in PL signal intensity was measured at different Si concentrations determined by Al/In ratio in the barriers.

We attribute this behavior to the reduction of the piezoelectric field in QWs with quaternary AlInGaInN barriers and/or modulation doping. The obtained results are in a good agreement with the calculations of piezoelectric fields and overlap integrals for optical transitions. The extracted built-in electric fields for AlGaInN/InGaInN with 15 % of Al and 20 % of In are as high as 10^6 V/cm. The incorporation of up to 15% of In in the barrier reduces the field to approximately $3-5 \times 10^5$ V/cm. The optimized modulation doping reduces the built-in field below 10^5 V/cm.

Our results show that combination of Energy Band/Strain engineering with modulation doping of the structures allows smooth tuning of emission wavelength and enhancement of emission efficiency.

We will also present the results of our studies of the p-type doping of AlGaInN/InGaInN layers, heterostructures, and quantum wells. Several approaches of p-dopant activation will be described.

Superlattice Doping: Pros and Cons

Umesh Mishra

Abstract not available at time of publication.

Current Results and Future Potential of Doped p-type AlGaIn/GaN Superlattices

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Enhanced hole concentrations in the 10^{18} cm^{-3} range at room temperature are demonstrated in p-type AlGaIn/GaN superlattices. Capacitance-voltage measurements reveal concentrations in the high 10^{18} cm^{-3} range at room temperature, consistent with Hall effect data. Optical emission experiments on doped AlGaIn/GaN superlattices display a strong emission band below the bandgap of the GaN well layers, indicating the presence of strong electric fields in the superlattices. The comparison the emission energy with theoretical calculations yields an electric field in the GaN well layers of $4 \times 10^5 \text{ V/cm}$. The magnitude of the internal electric field depends on the Al content of the superlattice. This dependence suggests that the field is caused in part by piezoelectric effects. Ohmic contacts to the doped superlattices have specific contact resistances in the high 10^{-4} Ohm cm^2 range. We also report on a novel type of ohmic contact that employs internal electric fields to enhance the tunneling current thereby reducing the specific contact resistance.

Electron Transport in GaN/AlGaN Structures

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The principal, novel feature of nitride structures is that an electron population can be induced by spontaneous and piezoelectric polarization without the necessity for donor impurities to be added. A simple model for this will be presented. Although there will always be a background of unwanted defects of one sort and another, their contribution to the scattering of electrons can, in principle, be ignored in estimates of the mobility in the ideal case. The scattering rate in the bulk binary is then determined by phonons alone, limited by the symmetry of the conduction band to the polar interactions with LO optical and LA and TA acoustic phonons and by the deformation-potential interaction with LA acoustic phonons. In the case of holes, all types of mode can participate, and this, plus the bigger effective mass, means that the mobility of holes will be at least an order of magnitude smaller than for electrons. For quasi-2D transport an additional scattering mechanism will arise from interface roughness, and in the case of alloys there will be scattering from fluctuations in the composition.

All these scattering mechanisms remove momentum and energy from the electron gas and are the principal source of electrical resistance. Mobility, however, is a property of the whole electron distribution, and this can be affected by degeneracy and by electron-electron scattering. This is a particularly important effect in the case of the high electron concentrations induced by polarization. A rise of Fermi level will, for example, increase the population of electrons that can emit LO phonons, and this will reduce the mobility. On the other hand, electron-electron scattering tends to produce a drifted distribution that increases the drift velocity, and this effect opposes the reduction due to degeneracy. A third factor is screening. The reduction of scattering rate produced by screening is greatest for the interaction with acoustic modes, particularly the piezoelectric interaction, because the plasma frequency of the electrons is usually much higher than the frequency of the acoustic modes, and therefore the electrons can respond virtually instantaneously. The effect on the optical phonon interaction is more complex. The screening in this case is dynamic and it may even enhance the interaction for certain phase differences when the plasma frequency and the phonon frequency are in near coincidence, leading to coupled plasma-phonon modes. In the case of the dense polarization-induced gases in AlGa_N/Ga_N structures, all of these effects must be taken into account in any estimate of mobility. The results of an estimate of the electron mobility in an AlGa_N/Ga_N FET will be presented along with estimates for bulk Ga_N and bulk AlGa_N.

Although technologically less important to calculate, the mobility in AlGa_N, being in principle determined in part by alloy fluctuations, introduces an old problem: what is the scattering potential? the difference of bandgaps of the constituent binaries? the difference of electron affinity? the difference of polarity? If polarity, alloy scattering is negligible, since Al and Ga are almost equally polar. Otherwise, alloy scattering is significant. There is a problem here.

There are many transport phenomena in the nitrides that have yet to be explored. The obvious ones are the electron-transfer NDR and the acoustoelectric effect. A third, rendered possible perhaps by the large bandgaps and high breakdown fields of the nitrides, is the appearance of Bloch oscillations in bulk material and associated Wannier-Stark quantization. Some preliminary theoretical results on this will be presented.

This work on transport was supported by the Office of Naval Research (N00014-96-1-0998 monitored by Dr. Colin Wood, and Muri N00014-96-1223 monitored by Dr. John C. Zolper) and the Engineering and Physical Science Research Council (EPSRC GR/L 56725).

High Field Transport Calculations in 4H-SiC

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We present the first comprehensive theoretical study of the hole initiated impact ionization process in 4H-SiC. It is accepted knowledge that the holes dominate impact ionization induced breakdown in 4H-SiC. Though multiple groups have made experimental measurements of the ionization coefficients, little is currently known concerning the anisotropy of the ionization coefficients. In addition, the physics of high field transport in SiC is not well understood. Here, we present the first determination, either experimental or theoretical, of the directional dependence of the hole initiated ionization coefficient. It is found that there exists a significant anisotropy in the ionization coefficient for fields applied parallel and perpendicular to the c-axis direction. Good agreement with experimental measurements of the hole initiated ionization coefficient for fields applied along the c-axis direction is obtained provided that the holes can move between bands in the proximity of band intersection points via interband tunneling. Inclusion of interband tunneling in the present model is necessary in order to recover the experimental results. If interband tunneling is not included within the model, the calculated ionization coefficients are orders of magnitude lower than the experimental measurements.

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Laser Spectroscopy of Doping and Carrier Dynamics in WBG Semiconductors

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Our talk will focus on two problems relevant to this workshop, carrier dynamics in InGaN and doping of SiC.

The role of indium alloy fluctuation in InGaN is the subject of considerable interest. We have used time-resolved photoluminescence to investigate the role of indium alloy fluctuations and the associated disorder in InGaN films, multiple quantum wells, and LEDs. Typically the PL decay kinetics are well described by a stretched exponential.

$$\exp(-(t/\tau)^{\beta})$$

The observation of stretched exponential kinetics is typical of disordered media. The wavelength dependence of the stretched exponential lifetime, τ , and stretching parameter, β , indicate that the carriers migrate between different nanometer scale regions of high indium concentration on the time-scale of the excited state lifetime. Simple physical models allow for the estimation of the typical length scale of the alloy fluctuations. The temperature dependence of the stretched exponential decays allows for the estimate of the magnitude of band gap fluctuation associated with the alloy disorder.[1]

SiC is commonly n-type doped with nitrogen. Although this is well established as a viable doping methodology the microscopic mechanisms are not well understood. Electronic Raman scattering can be used to investigate shallow nitrogen energy levels due to valley-orbit splitting in SiC. Typically n-type SiC is green due the presence of absorption bands in the near IR. Recently we have discovered that the electronic Raman scattering can be significantly enhanced by the excitation into the NIR absorption bands.[2] The use of resonance effects allows for the detection of the electronic Raman scattering at room temperature. At high nitrogen concentrations, the onset of metallic behavior can be observed by the broadening and decreasing Raman shift of the electronic Raman transitions. Similar effects have been previously observed in silicon and germanium.

Some of this work was done at Rutgers University. Collaborators include:

M. Pophristic, J. Burton, Rutgers University
A. Gupta, M. Yoganathan, J. Whitlock, T. Anderson, LittonAirtron
C. Tran, R. Karlicek, and I. Ferguson, EMCORE Corporation

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Carrier Dynamics in Schottky Diodes

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III-V nitride semiconductor materials are good candidates not only for short wavelength optical devices but also for high power electronic devices. Since rich Al contents ternary layers of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x > 0.5$) have large energy-gaps, those materials are further suitable for high power electronic devices. However, as the Al contents are increased, the conductivity becomes low and the power dissipation of the Joule heat are increase.

We have investigated the Schottky junction between high rich Al contents ternary layers of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and metals by fabricating Shottky diodes. The electron current in the diodes are controlled, using the band engineering varying the Al contents in the ternary layers. The components of the ternary layers are studied by the Auger Electron Spectroscopy. The Shottky barrier heights and the ideal factors are measured by the I-V characteristics. Since it is hard to obtain the good quality ternary layers with high Al contents. We will present the relation between the surface structures and the electronic characteristic and propose a new power device using the ternary layers of rich Al contents $\text{Al}_x\text{Ga}_{1-x}\text{N}$.

HVPE-grown GaN Avalanche Photodiodes

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and I. L. Melngailis

We describe results for linear-mode operation of GaN avalanche photodiodes (APD's) with spatially uniform gain over a 37 μ m-diameter device area. The APD's were fabricated from HVPE-grown GaN layers that included a Si-doped n⁺ layer for electric-field confinement, an as-grown n-layer for the multiplier, and a Zn-doped layer for the cathode. Both planar and mesa-etched devices were fabricated using SiO₂ passivation and Ti/Au metallization to the layer. Device simulations and forward bias current-voltage characteristics show that the Zn-doped acceptors exhibit sufficient ionization at room temperature to not inhibit device performance. Linear-mode gains of 10 with spatial variations < 10% were achieved with measured yields of 7 out of 12 devices measured in a single sample. The best mesa-etched devices had low leakage current densities ($\sim 10^{-7}$ A/cm²) near unity gain ($V_{dc} = -20$ V) that rose to between 10^{-4} - 10^{-5} A/cm² near gain of 10 ($V_{dc} = -90$ V). These devices exhibit classical Geiger-mode operation when they are pulse-biased above breakdown and are exposed to highly-attenuated UV illumination at $\lambda = 325$ nm. These initial Geiger-mode trials indicate that there is a strong dependence on both the photon-detection efficiency (PDE) and the dark-count rate on the overbias, as seen in other semiconductors.

Visible and Infrared Luminescence from Er-doped GaN Films

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The luminescence properties of erbium doped gallium nitride are of significant interest for potential applications in full color displays and optical communications. We are currently investigating the photoluminescence (PL) properties of Er doped GaN prepared by solid-source molecular beam epitaxy. This paper focuses on the green (537 and 558 nm) and infrared (1.54 μm) $4f\text{-Er}^{3+}$ transitions. 1.54 μm infrared Er^{3+} PL was observed under both, above (325 nm) and below (442 nm) gap excitation. The lifetime of the 1.54 μm PL was measured to be ~ 2.3 ms at 15 K and decreased to ~ 1.9 ms at room temperature. At higher temperatures (~ 500 K) the lifetime continued to decrease most likely due to nonradiative decay. In addition to infrared luminescence, optical excitation at 325 nm also resulted in the observation of a broad-band PL spanning from ~ 450 -700 nm and two intense green Er^{3+} lines at 537 nm and 558 nm. Under below-gap excitation at 442 nm, the visible PL was dominated by the broad-band and the green Er^{3+} lines were hardly observable. Resonant Er^{3+} excitation at ~ 495 nm, however, resulted in the observation of green lines with an average lifetime of ~ 10.8 μs at 15 K and ~ 5.5 μs at room temperature. The decrease in lifetime is attributed to an increased radiative decay rate resulting from the thermalization of two excited states ($^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$). A detailed analysis of the visible and infrared Er^{3+} PL from GaN:Er in view of possible opto-electronic applications will be presented.

Doped GaN Quantum Dots

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GaN dots have been grown on c-plane sapphire, HVPE grown GaN on sapphire, and (111) Si substrates by reactive and combination of RF and reactive molecular beam epitaxy. A relatively new method involving two-dimensional growth followed by a controlled interruption during which dots were formed was employed. Due to localization and large dot density, relatively high luminescence efficiencies were obtained on both substrates. Both red and blue shifts were observed. Single layer dots were used for AFM analysis whereas 30 layer dots were used for photoluminescence experiments. AlN wetting layers, some too thick for mechanical interaction between stacks, and some thin enough for vertical coupling were used. Details of the optical processes in the dots will be presented.

P-type Superlattice Doping: Material Characteristics Pertaining to Bipolar Devices

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The use of wide band gap (WBG) semiconductors such as GaN and SiC has proven to result in superior electron device performance for microwave applications. Unipolar electron devices based on WBG heterostructures, such as AlGaIn/GaN HFETs can deliver microwave powers over 10 W/mm with high power-added efficiency (PAE), f_t and f_{max} [1]. These devices have already outperformed Si-based counterparts, which are represented by LDMOS technology. HBT devices are known to possess fundamentally superior figures of merits as compared to unipolar HFETs. The technology of AlGaIn/InGaIn LEDs, which is based on p-n diodes, is quite mature. However, technology of HBTs, which is also based on p-n heterojunctions, is still at its initial development stage.

The key problem with demonstrating high performance HBTs in AlGaIn/GaN material system is a poor conductivity of the p-GaN layers, which are used in a thin base. This results in a high base access resistance and ohmic contact resistance, translating into low gains and high microwave parasitics.

To enhance hole conductivity in the base, we proposed to use p-AlGaIn/GaN superlattice structures [2]. Even though high lateral conductivity was demonstrated in such structures, due to proposed modulation doped mechanism [3], the vertical conductivity across the superlattice layers, which is important transport characteristics of vertical HBT devices, has not yet been studied.

The minority carrier diffusion length, L_D , is an important material characteristic of the HBT base, affecting the device design and overall performance. Line-scan EBIC measurements can be used to determine the diffusion length.

We present and analyze new experimental data on the *lateral* and *vertical* minority carrier diffusion length, L_D , in bulk p-GaN and p-type $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ SL structures with different Al compositions and geometries. Line-scan EBIC measurements are used for the diffusion length measurements. The measurements are taken at an accelerating voltage of 10 kV and at magnifications of x 25,000 and x 150,000 for the planar and cross-sectional EBIC respectively. We obtain the planar diffusion length of $L_D \sim 0.26 \mu\text{m}$ and the cross-sectional $L_D \sim 0.1 \mu\text{m}$, resulting in a lateral/vertical L_D ratio of 2.6. Strategies to reduce this ratio by increasing vertical diffusion length, for example using graded superlattice structures, will be discussed.

I-V characteristics and transport data on p-n junction diodes with p-type superlattice anodes are analyzed. Experimental measurements of the vertical minority carrier diffusion length in superlattice-based p-n diodes will be also presented and discussed.

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Influence of Dopants on Defect Formation in GaN; Bulk and MOCVD Grown Samples

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Transmission electron microscopy (TEM) has been applied to study defects in doped and undoped bulk GaN grown from Ga melt under hydrostatic pressure of Nitrogen and also in epitaxial layers grown by MOCVD on sapphire substrates. An influence of Mg and In have been studied.

Mainly p-doped samples with Mg will be discussed. Three types of samples are considered: bulk samples where Mg was added to Ga melt under high hydrostatic pressure of Nitrogen and two types of MOCVD grown samples: one with Mg delta doping and the second with a continuously Mg doped layers. In all three types of samples a high concentration of Mg ($6 \times 10^{19} \text{ cm}^{-3}$) was present.

The TEM studies show formation of Mg rich defects but their atomic structure differs depending on crystal growth polarity. For growth with N-polarity spontaneous ordering of Mg rich planar defects has been observed. These defects are monolayers of cubic structure formed on basal planes separated by 10 nm along the c-axis. These planar defects have characteristics of stacking faults but also show the characteristics of pairs of inversion boundaries. Similar planar defects were observed in MOCVD samples with Mg delta doping at the beginning of Mg introduction. Further growth then shows the Mg-rich defects characteristic for growth with Ga polarity similarly as in bulk crystals growing in the Ga to N polar direction. These defects are three dimensional Mg-rich pyramids. Growth in the Ga polar direction is an order of magnitude faster.

In addition to Mg doped samples bulk GaN samples with In added during growth were studied and compared to those grown by MOCVD. Growth of In doped bulk samples with N polarity leads to undulated surface as was observed for Mg rich samples. This undulation was observed for undoped samples for growth with Ga polarity. Some planar defects were observed in In rich samples but ordering was not observed. These samples were also compared to MOCVD grown samples of different In contents.

If time allows influence of oxygen will be also discussed.

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Valence Control by Codoping in Wide Band-gap Semiconductors (GaN, AlN, ZnSe, ZnO): Prediction vs. Experiment

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It is well known that the fabrication of both low-resistivity n- and p-type wide band-gap (E_g) semiconductors is difficult (uni-polarity or mono-polarity), because of the so called compensation and deep acceptor levels in the wide band-gap semiconductors, such as ZnSe ($E_g = 2.7$ eV), ZnO ($E_g = 3.4$ eV), GaN ($E_g = 3.4$ eV), and AlN ($E_g = 6.2$ eV). The origin of the difficulty to fabricate the low-resistivity wide band-gap semiconductors are (i) the compensation and (ii) the deep energy levels of acceptors with increasing E_g (decreasing the dielectric constant), for example, ZnSe:N (90 meV), ZnO:N (300 meV), GaN:Mg (200 meV), and AlN:C (500 meV). In order to fabricate the low-resistivity p-type materials, (i) we should avoid compensation with increasing solubility of the dopant (reducing the formation energy of the dopants), and (ii) we should reduce the energy level of acceptors upon doping.

To do so, we propose an effective new valence control method, which is so called the codoping method (using both n- and p-type reactive codopants at the same time), for the fabrication of low-resistivity p-type GaN, AlN, ZnSe, and ZnO based upon ab initio electronic structure calculations. We find that the codoping method forms acceptor and donor complexes during the MBE or MOCVD crystal growth, and contributes (i) to reduce the formation energy of the dopant due to the reduction of the lattice relaxation energy and Madelung energies, because the acceptor-donor size compensate and the attractive acceptor-donor interaction overcomes the repulsive ones, and (ii) to increase the carrier mobility due to the short-range dipole scattering (long-range Coulomb interaction is dominated in the case of simple doping), and (iii) to reduce the energy level of acceptors due to the formation of donor and acceptor complexes (a donor level is raised and an acceptor level is lowered with forming donor-acceptor complexes).

We review our new valence control method of codoping for the fabrication of low-resistivity p-type GaN, AlN, ZnSe, and ZnO, which is proposed by ab initio electronic structure calculations [1-11]. We propose the following codoping method (using both n- and p-type reactive dopants at the same time) to fabricate a low-resistivity p-type semiconductors; (1) GaN: [SiGa+2MgGa(or BeGa), H+2MgGa(or BeGa), and ON+2MgGa(or BeGa)], (2) AlN: [ON+2CN], (3) ZnO: [GaZn+2NO, AlZn+2NO, and InZn+2NO], and (4) ZnSe: [InZn+2NSe, ClSe+2NSe, 2LiZn+ClSe (or ISe), and TeSe+2NSe]. We compare our predictions of codoping with the recent successful codoping experiments for the fabrication of the low-resistivity p-type wide band-gap semiconductors. We also discuss how to fabricate a transparent super-ferromagnet based upon ZnO [12].

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Recent Progress in the Low Temperature Growth of GaN by Combined Laser Induced and Plasma Assisted Chemical Vapor Deposition

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Low temperature excimer laser and microwave plasma assisted chemical vapour deposition (LCVD) is based on a conventional thermal MOCVD process, but allows deposition of GaN, at temperatures in the range of 400 - 600C. The laser dissociates trimethylgallium and ammonia photolytically to produce reactive Ga and nitrogen radicals which, in turn, form GaN on the substrate. A remote microwave ammonia plasma is used to inject additional active nitrogen radicals to ensure stoichiometry. Growth commonly takes place on silicon, GaAs or quartz either directly or on an AlN buffer. Growth on other substrates is also possible. The LCVD technique yields films of good structural, optical and electrical quality. In the films grown on quartz most crystallites are oriented along (0002), while growth on sapphire yields a mixture of crystallites oriented along (0002) and (11 $\bar{2}$ 0). Some traces of (11 $\bar{2}$ 2) orientation are present in both. Films up to 12 microns thick have been grown and separated from substrates using standard lift-off methods. Piezoelectric properties of GaN and AlN films have been measured by an interferometric method.

In n-type films, mobilities of up to 400cm²V⁻¹s⁻¹ (at 150K) are observed at growth temperatures below 600C, while electron concentrations between 10¹⁴cm⁻³ and 10¹⁸cm⁻³ can be controlled by selecting the III-V ratio during growth. P-type doping without post-growth activation is feasible using standard bis-cyclopentadienylmagnesium precursor and by introducing Mg vapor directly into the injected microwave plasma.

In n-type films a strong PL band occurs at 3.2 eV, yellow emission has also been observed. In p-type films the blue band is also present. Raman scattering in n-type films reveals the presence of microcrystallites in the order of 7 nm. Photoconductive decay in n-type films shows two time constants of 0.8 and 6 s, these corresponded to 3.5 orders of magnitude change of conductivity in less than 1 s.

The LCVD method can also be applied to In_xGa_{1-x}N and Al_yGa_{1-y}N with compositional parameters x up to 0.4 and y up to 1. Chemically stable AlN has been grown at room temperature with resistivity up to 10¹⁶ cm.

Defects and Doping in Group-III Nitrides

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First-principles methods have had a major impact in describing the properties and interaction of defect and impurities in group-III nitrides and give a detailed insight into various doping issues. In the first part we will briefly summarize our present understanding about native defects in GaN. Vacancies are found to be the dominant native defects: under p-type conditions the nitrogen vacancy (a single donor) has the lowest formation energy, under n-type conditions it is the Ga vacancy (a triple acceptor). Thus, nitrogen vacancies are a likely compensating center for acceptor doping.

In the second part we will focus on the role of hydrogen in doping of GaN. Based on detailed first-principles calculations we identify the microscopic mechanism of how hydrogen affects the Mg acceptor doping in GaN, how it can be used to control and increase the acceptor concentration and what are the limits for this process. Finally, we apply the same formalism to alternative acceptors in GaN. Specifically, the suitability and efficiency of a wide variety of alternative acceptor impurities (Be, Zn, Ca, Li, Na, K) will be discussed. Our results show that none of these impurities performs better than Mg with respect to solubility, low ionization energy, and stability against self-compensation. Only Be has a comparable solubility but it may suffer from compensation due to incorporation on interstitial sites.

Native Defects in SiC

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SiC is an attractive candidate for high temperature and high power semiconductor devices applications. The behavior of impurities during growth and during post-growth and post-implant anneals depends sensitively on their interaction with native defects. Although there has been some previous theoretical work on native point defects in SiC, these studies have stopped short of predicting the density of native point defects. In this work we have identified the native defects in SiC as a function of equilibration temperature and carbon chemical potential within the two-phase region. The carbon and silicon antisites are found to dominate under carbon-rich and silicon-rich conditions, respectively. The carbon vacancy is also present at concentrations in excess of $10^{10}/\text{cm}^3$ and it is the only defect that predominantly ionized under the conditions considered. At the equilibration temperatures considered, only the carbon vacancy density is impacted by the presence of donors or acceptors.